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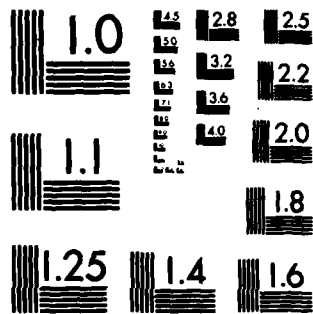
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FINAL REPORT

AFOSR-82-0137

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Study of the Interaction of Hydrazine, Methylhydrazine,  
and Unsym-dimethylhydrazine with Porphyrins, Metalloporphyrins  
and Some Metal Coordination Compounds

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## Item 20 (Cont)

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Trisodium pentacyanoferrate (TPF) forms derivatives with hydrazine, methylhydrazine, and unsym-dimethylhydrazine. Each of these derivatives are similar in color and each of the derivatives have similar visible spectra. Separation of these derivatives by HPLC could offer a rapid analytical method of determining the composition of mixtures of the hydrazines. The photoreduction of Zn-tetraphenylporphyrin (Zn-TPP) with hydrazine, methylhydrazine, and unsym-dimethylhydrazine in pyridine was investigated. Results indicate that the presence of hydrazine in mixture with methylhydrazine, and unsym-dimethylhydrazine can be confirmed due to the formation of a unique color that is not produced when Zn-TPP is photoreduced with methylhydrazine, and unsym-dimethylhydrazine. Organometallic compounds more sensitive to reduction by hydrazine and porphyrin derivatives that may possibly form hydrazone derivatives with hydrazine are currently being investigated.  
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## FINAL TECHNICAL REPORT

**TITLE:** A Study of the Interaction of Hydrazine, Methylhydrazine, and Unsym-dimethylhydrazine with Porphyrins, Metalloporphyrins and Some Metal Coordination Compounds

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**GRANT NUMBER:** 82-NC-039

**JUNIOR RESEARCH PERSONNEL:** Sonya Maxwell

### ABSTRACT

Trisodium pentacyanoferrate (TPF) forms derivatives with hydrazine, methylhydrazine, and unsym-dimethylhydrazine. Each of these derivatives are similar in color and each of the derivatives have similar visible spectra. Separation of these derivatives by HPLC could offer a rapid analytical method of determining the composition of mixtures of the hydrazines.

The photoreduction of Zn-tetraphenylporphyrin (Zn-TPP) with hydrazine, methylhydrazine, and unsym-dimethylhydrazine in pyridine was investigated. Results indicate that the presence of hydrazine in mixture with methylhydrazine, and unsym-dimethylhydrazine can be confirmed due to the formation of a unique color that is not produced when Zn-TPP is photo-reduced with methylhydrazine, and unsym-dimethylhydrazine.

Organometallic compounds more sensitive to reduction by hydrazine and porphyrin derivatives that may possibly form hydrazone derivatives with hydrazine are currently being investigated.

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# A STUDY OF THE INTERACTION OF HYDRAZINE, METHYLHYDRAZINE, AND UNSYM-DIMETHYLHYDRAZINE WITH PORPHYRINS, METALLOPORPHYRINS AND SOME METAL COORDINATION COMPOUNDS

## Introduction

In recent years the analytical detection and analysis of hydrazine (H) and its derivatives methylhydrazine (MH), and unsym-dimethyl hydrazine (UDMH) has received increased attention because of their uses as rocket and jet propellants, industrial and medicinal agents.

Various analytical methods such as titrimetric, spectrophotometric and gas chromatographic procedures have been widely used in the past. Many problems have been encountered using these methods, such as limited sensitivity, and long and extended derivatization steps needed to prepare samples for analysis. Research is ongoing in the area of developing more reliable analytical methods for use in hydrazine detection

## Detection Using Trisodium pentacyanoaminoferate (TPF)

Experimental efforts utilizing this method were concentrated in the area of determining an ideal solvent, temperature, and concentration level in the Thin-layer separation of TPF-hydrazine products.

Derivatives were prepared by pipetting 0.01 ml aliquots of each hydrazine into test tubes containing 5.0 ml of 0.1M aqueous TPF solution. The pH of the derivatized solutions were adjusted to remain in the range of 2.5 to 4.5 unbuffered with sulfuric acid or hydrochloric acid. This pH range was optimum in giving stable derivatives of TPF and hydrazines. Maximum derivative development occurs after samples are left to stand overnight or after approximately 9 - 12 hours.

The three TPF-hydrazine derivatives were mixed equally using 1 ml portions of each. The derivatives and underivatized TPF were spotted by means of a micropipette on cellulose Thin-layer (TLC) plates. The plates were activated at 105°C for 2 hours, then cooled to room temperature in a dessicator. After spotting, the plates were placed in a developing chamber containing a mixture of 60% acetonitrile and water. After a 15 cm ascend of the solvent front, the plates were removed and air dried at room temperature. Color of the migrated samples was intense and the use of UV light and/or oven drying of the plates was not needed to determine the location of the various hydrazine derivatives.



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The calculated  $R_f$  values of the TPF-hydrazine derivatives in mixture were in a 4.5% to 8% agreement with the  $R_f$  values of the TPF-hydrazine derivatives determined separately on TLC plates.

The quantitative determination of H, MH, and UDMH derivatives of TPF by High-Pressure Liquid Chromatography (HPLC) in mixture is being done in collaboration with Dr. H.G. Lovelagy of the School of Aerospace Medicine.

### Conclusions

Hydrazine-TPF derivatives have been previously reported in a colorimetric quantitative determination of UDMH. The method has not experienced wide use because of its less than adequate reliability and even less reproducibility. Studies of TPF-hydrazine derivatives that are separated by HPLC could offer a rapid method of quantitatively determining the composition of hydrazine mixtures as predicted by TLC results obtained in this study. Lastly, analytical methods involving two other iron containing coordination compounds very sensitive to slight reductions that also exhibit pronounced spectrophotometric changes upon reduction have been published in recent journals. Procedures using these compounds could offer an alternative spectrophotometric method of determining hydrazine.

### Detection Using Porphyrins and Metalloporphyrins

The photoreduction of Zn-tetraphenylporphyrin in pyridine using hydrazine, methylhydrazine, and unsym-dimethylhydrazine was studied to determine what products and/or derivatives result, and the degree of photoreduction each of the three hydrazines is capable of sustaining.

Similarly as reported by A.N. Sidorov et al., Doklady Akademi Nauk SSSR, vol. 158, no. 4, pp 973-976 ( 1964 ), the reduction of Zn-tetraphenylporphyrin with hydrazine ( $N_2H_4$ ) resulted in a rapid nearly non-observable reduced yellow form of the porphyrin, which changed to a green form after about 30 minutes. After 9 to 12 hours the yellow reduced form reappears and in some cases this reduced state is followed by a complete loss of color, most likely the complete destruction of the porphyrin cyclic ring. Sidorov's experiments were carried out initially in a system protected from exposure to air, then followed by exposure to air to oxidize the porphyrin. All observations in this study were carried out in air environments. This could account for differences in pathways of the photo-reduction reactions observed here and those reported by Sidorov.



Hydrazine produces a derivative of green color when reacted with Zn-tetraphenylporphyrin (Zn-TPP) in pyridine. After 30 to 40 minutes of exposure to direct light the color develops well enough to be observed looking at the light source through the sample. Similar, but less pronounced results are observed with methylhydrazine and unsym-dimethylhydrazine. No green color is observed with MH and UDMH, but after about 24-36 hours of continuous exposure to light, the reduced yellow color forms are apparent. The spectra resulting from the reaction of the three hydrazines with Zn-TPP are identical with respect to the yellow forms. No reductions of Zn-TPP by the hydrazines were observed in dark reactions.

Thin-layer separation with various solvents and solvent combinations (e.g. methyl alcohol, ethyl alcohol, acetonitrile, pyridine, tetrahydrofuran, and chloroform) of the three Zn-TPP photoreduced derivatives in mixture was not successful. Presently, Dr. H.G. Lovelady of the School of Aerospace Medicine is attempting a separation by HPLC.

### Conclusions

Results obtained in this study indicate a photoreduction method can be used as a preliminary screening technique to determine if hydrazine is present in mixtures with methylhydrazine and/or unsym-dimethylhydrazine.

Two porphyrins which have peripheral functional groups that have been shown to react with hydrazine and derivatives of hydrazines were synthesized. Tetraphenylporphyrin (TPP) was synthesized by the method of Alder et al., Journal of Organic Chemistry, Vol. 32, p476 (1967).

Sulfonic acid groups were added to TPP to form a water soluble porphyrin and sulfonyl chloride groups were added to TPP to form a non-water soluble porphyrin. Hydrazine, methylhydrazine, and unsym-dimethylhydrazine were added to samples of both porphyrins in various solvents at several pH levels. No physical changes were observed and no significant spectra changes occurred that would indicate peripheral reaction of the porphyrins with hydrazine or its derivatives. Only in low pH solutions of nonmetalloporphyrins or the free base form was there an exhibition of acid/base spectra changes as is predictable.

A porphyrin derivative of TPP with peripheral carbonyl groups has yet to be synthesized. Syntheses were attempted without success to make this compound by acylating the peripheral phenyl

groups of TPP. Another approach yet to be tried is to synthesize an aldehyde with an acyl group. This aldehyde will be condensed in a reflux reaction with pyrrole as described by Alder, et al.. This cyclization reaction could possibly yield a prophyrin that may react selectively with hydrazines.